

TECHNICAL MEMORANDUM

TO: Mike Sinclair – MeadWestvaco Rumford Mill

FROM: Steve Woodard, Ph.D., P.E. - Woodard & Curran

DATE: February 19, 2003

RE: **Bench-Scale Phosphorus Removal Testing**

Executive Summary

MeadWestvaco requested engineering assistance related to on-site bench scale testing and development of an operating cost estimate for modifications to their treatment system. The modifications would be focused on reducing effluent wastewater phosphorus to levels below 0.25 mg/l. The phosphorus removal system would only operate in the summer months to help limit algae growth in the receiving water. The typical algae growth starts in the beginning of June and trails off rapidly in October. The cost estimate includes treatment from May 15th to September 30th each year to account for a travel time of roughly two weeks in the Androscoggin River.

Woodard & Curran (W&C) performed bench testing at MeadWestvaco's Rumford mill on January 24, 2003. The goals of the testing were to: (1) determine the approximate ferric chloride dose required to reduce the Mill's effluent to less than 0.25 mg/l; (2) determine the amount of sodium hydroxide required to neutralize the mixed liquor after ferric chloride addition; and (3) to estimate the annual operating costs associated with ferric chloride addition, caustic addition, and sludge disposal.

The bench-scale testing results demonstrate that ferric chloride is effective in removing phosphorous from the mill's wastewater. The cost to remove phosphorus to levels below 0.25 mg/l levels is estimated between \$3 and \$5 million per year in chemical and sludge disposal costs.

It is recommended that, if a 0.25 mg/l total P limit were to be imposed on the mill, full-scale tertiary filtration would be required to guarantee consistent compliance with that limit. Since microbes contain P in their cell mass, such a limit would necessitate very high levels of consistent TSS removal. The capital cost of such a tertiary treatment system would range from \$15 to \$45 million, depending on design conditions and equipment selection.

Introduction

Steve Woodard, Andy Bishop and Kim Crouse, all of Woodard & Curran, visited the mill January 24, 2003 to perform bench-scale P removal testing. The primary objective of the visit was to add varying doses of metal salt to mixed liquor samples to examine the effectiveness of phosphate precipitation and co-precipitation to reduce effluent P levels below 0.25 mg/l. Ferric chloride was the metal salt used to facilitate the precipitation reactions in the bench-scale trials.

Plant Conditions

The treatment plant generally runs at approximately 0.8 mg/l reactive phosphorus in the secondary effluent. The reactive phosphorus was measured at 0.5 mg/l on the day of the bench scale tests. The samples were adjusted accordingly by adding 0.3 mg/l P, using a standard phosphate solution, to represent typical operating conditions at the treatment plant.

It is important to have excess soluble, reactive P (orthophosphate) on the order of 0.5 to 1.0 mg/l in the mixed liquor to promote healthy biological growth and flocculation. Total P refers to the combination of orthophosphate (PO_4^{3-}), suspended P (e.g. associated with solids), and polyphosphate. Polyphosphates are long chain, soluble P compounds sometimes used in detergents. The vast majority of detergents in use today are readily biodegradable, and any polyphosphate is quickly broken down to orthophosphate in the aeration basin.

Materials and Methods

Mixed liquor samples were obtained from the secondary clarifier head box. The mixed liquor was thoroughly mixed and dispensed into six 2-liter Phipps & Bird beakers. The following general stepwise procedure was adhered to for all of the testing performed.

1. 0.3 mg-P/L of phosphate standard was added to each of the beakers.
2. The beakers were stirred for 5 to 10 minutes.
3. The phosphorous removal agent (ferric) was added at five different concentrations. The sixth beaker was a control, with no ferric added.
4. The beakers were mixed for approximately 15 additional minutes.
5. 1.54 N sodium hydroxide was added (if needed) to adjust the pH of each beaker back to 7.0 Standard Units (S.U.).
6. After settling under quiescent conditions for 30 minutes, the supernatant was sampled using a 5-ml syringe.
7. The sample was either analyzed directly, or filtered through a 0.45 μm filter to remove bacteria, depending on the test being performed.

The pH of the wastewater was measured with a WTW portable pH meter. The pH probe was calibrated approximately every four hours, or as needed, using pH standard solutions (4 and 7).

The metal salt ferric chloride, a well known phosphorous precipitation chemical, was tested for phosphorous removal effectiveness at the mill. Stock solutions were made by adding known amounts to tap water (Appendix A contains the field data and pertinent information). Ferric chloride is a Lewis acid, which means when added to wastewater, it uses up alkalinity and can cause the pH to decrease. As such, the pH of the wastewater was adjusted, if needed, after metal salt addition to 7.0 using 1.54 N sodium hydroxide.

Onsite total P analysis was performed using the Test'N Tube™ method from HACH (Method 8190). The method consists of oxidizing the sample with potassium persulfate, heating to 150 °C for 30 minutes, allowing it to cool to room temperature, adding caustic, zeroing the spectrophotometer, adding a reagent pillow (PhosVer 3), waiting 2 minutes for the colorimetric reaction to fully develop, and then recording the concentration. The filtered samples were analyzed to examine the P contribution of biological solids contained in the final effluent, in addition to the dissolved fraction. Control of effluent TSS is important since it will contribute varying amounts of total P to the effluent, depending on the volatile fraction and the TSS concentration. Figure 1 shows, on a theoretical basis, the impact that suspended solids can have on total P concentration in the final effluent. Figure 1 also demonstrates that it would very be difficult to maintain consistent compliance with a 0.25 mg/l total P limit without the use of tertiary filtration. Any blip in secondary TSS removal would run the risk of causing an exceedance, even with the use of ferric chloride to precipitate soluble P.

Onsite reactive P analysis was performed using the Test'N Tube™ method from HACH (Method 8048). The method consists of: zeroing the spectrophotometer, adding a reagent pillow (PhosVer 3), waiting 2 minutes for the colorimetric reaction to fully develop, and then recording the concentration.

Results and Discussion

Two raw samples of MLSS were tested for total P and reactive P without adding phosphate or ferric chloride. The purpose of testing these duplicate samples was to provide a rough check of the repeatability (precision) of the P analyses before beginning the jar tests. The results for the reactive samples both read 0.54 mg-P/l and results from the total samples read 0.99 and 0.98 mg-P/l.

To determine the accuracy of the test, a sample was spiked with 0.6 mg-P/l of the stock solution without adding ferric chloride. The spiked sample was tested using the reactive P method. The result of the spiked sample was 1.12 mg-P/l, which accounts for 0.54 mg-P/l present in the raw sample and 0.6 mg-P/l added from the stock solution. The laboratory results are likely accurate to +/- 0.05 mg/L, based on the testing and measuring equipment used.

Figure 2 shows the removal of total phosphorus from the MLSS supernatant using different concentrations of ferric chloride. The actual data is plotted along with a line representing the “best fit” nonlinear regression. The samples were dosed with ferric chloride with concentrations up to 250 mg-Fe/l. The ferric chloride showed removal of total P from 1.23 mg-P/l in the raw sample down to 0.09 mg-P/l in the settled supernatant. As expected, P removal efficiency becomes exponentially less efficient with increasing ferric chloride dose once the P concentration drops below roughly 1 mg/l. In other words, Figure 2 shows the diminishing return associated with high levels of P removal from the Mill’s effluent.

Figure 1. Theoretical Increase in Effluent Total P from TSS, as a Function of Concentration and Percent Volatile

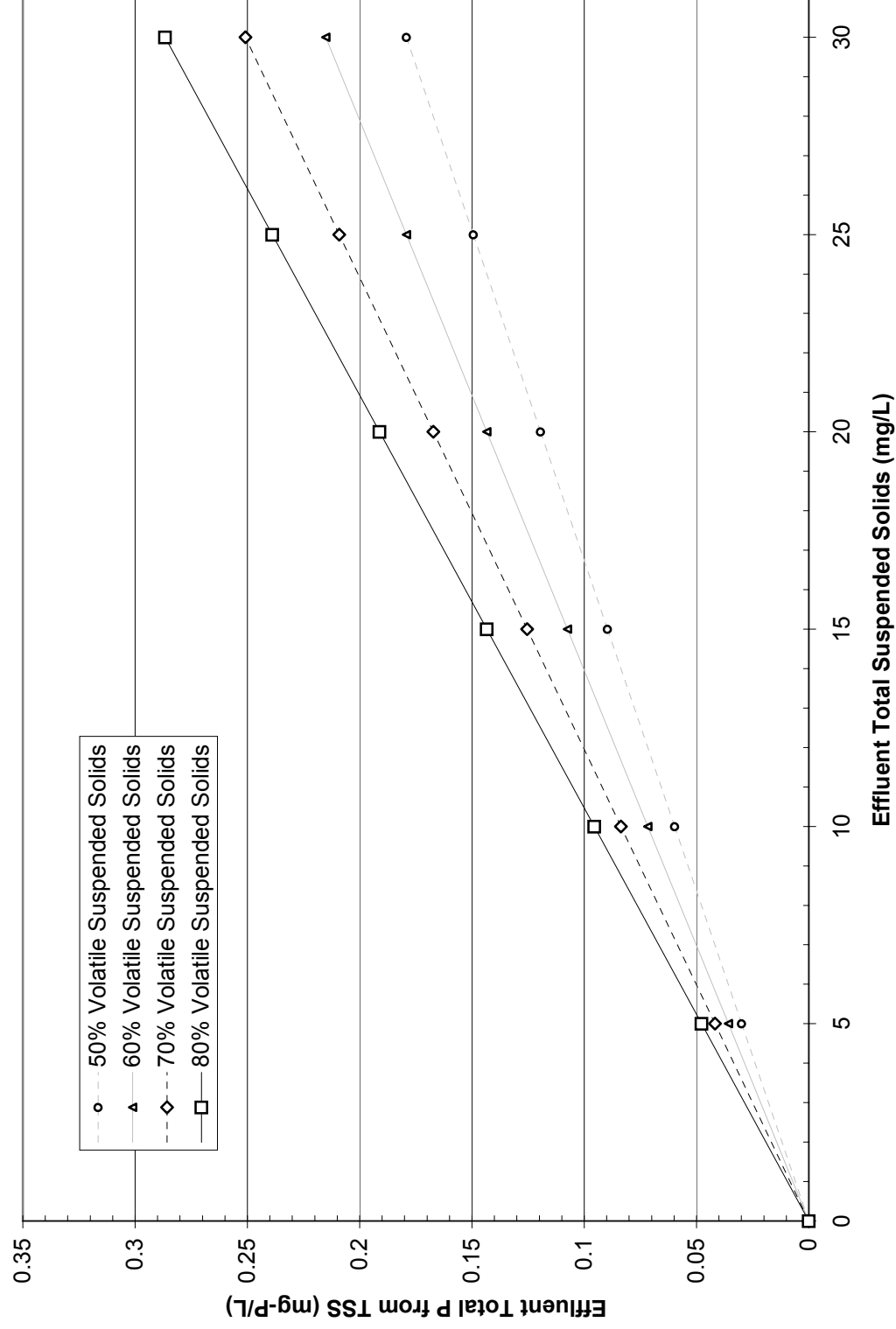


Figure 2: Total Phosphorus Removal

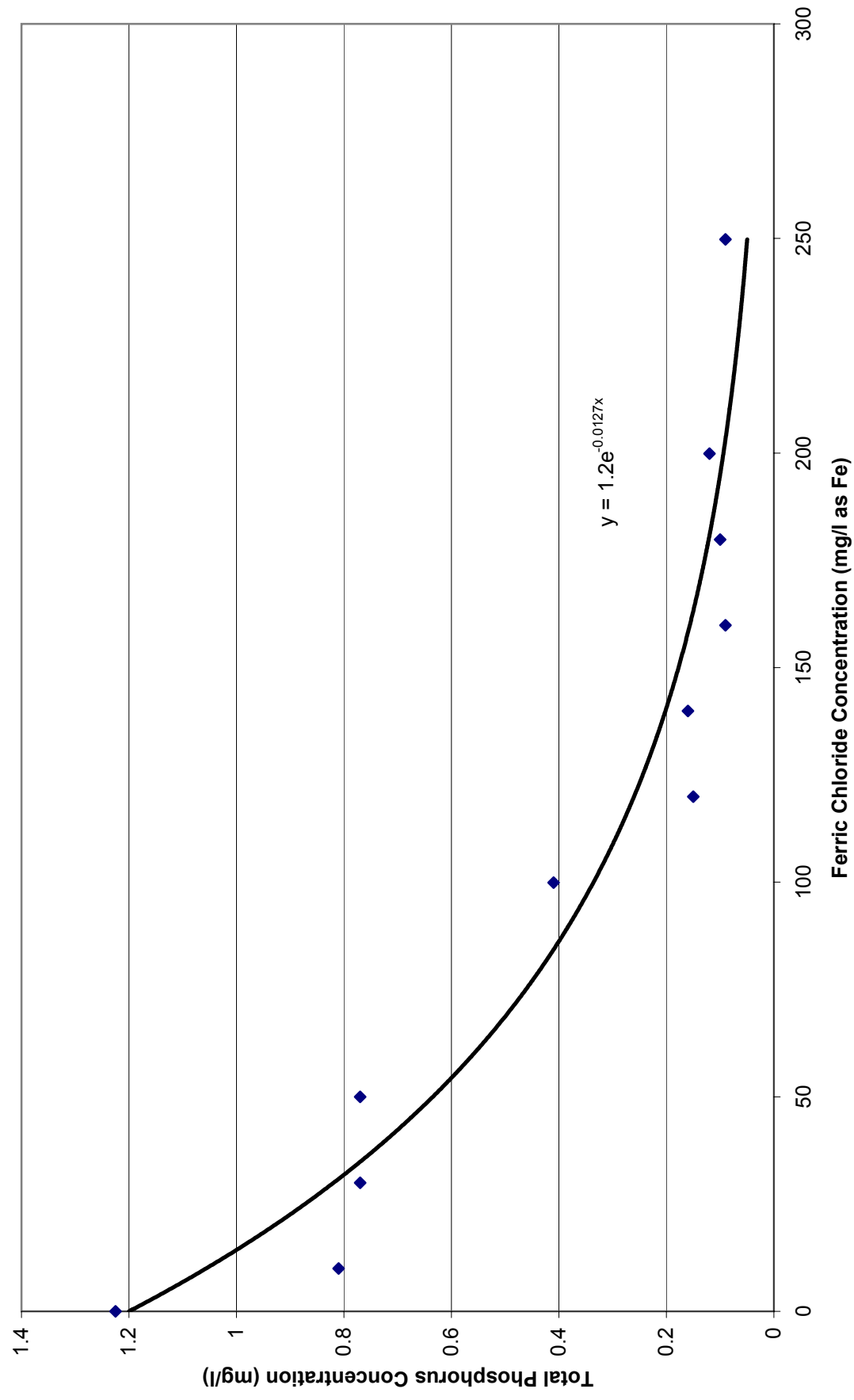


Figure 3 shows the removal of total phosphorus from filtered MLSS supernatant samples using different concentrations of ferric chloride. The samples were dosed with ferric chloride concentration up to 250 mg-Fe/l. The ferric chloride successfully reduced filtered P levels from 1.03 mg-P/l in the raw sample down to 0.04 mg-P/l at the higher doses. The total phosphorus removal of the filtered samples appears to level off at a dose of around 100 mg-Fe/l.

The bench scale testing also demonstrated that the addition of ferric chloride decreased the settling rate of the mixed liquor. The sample that was dosed with 120 mg-Fe/l settled 30 percent slower than the control beaker. The 180 mg-Fe/l sample settled 45 percent slower than the control.

Cost Estimate

Operational Costs

The preliminary cost estimate for the phosphorus removal system presented below includes only chemical addition costs and sludge disposal costs. Capital costs for pumps, piping, chemical storage, etc. are not included. It should also be kept in mind that these cost estimates are based on just one set of laboratory testing. Full scale testing for a period of several weeks would be required to verify these preliminary cost estimates.

The amount of ferric chloride needed was estimated from Figure 2. Based on a limit of 0.25 mg-P/l, the concentration of ferric would need to be roughly 120 mg/l. In reality, the treatment plant would want to operate at a level of approximately half the limit value (0.125 mg-P/l), in order to maintain a reasonable safety factor to accommodate day-to-day variations in wastewater character, treatment plant performance, etc. The ferric dose would have to be roughly 180 mg/l to reduce the effluent to 0.125 mg-P/l. The cost estimate includes costs for both levels of treatment, 120 mg-Fe/l and 180 mg-Fe/l.

The cost estimate for the proposed treatment system was based on the following assumptions:

1. The treatment system would operate from May 15th to September 30th each year (~140 days).
2. The flow rate is 34 MGD as stated in the effluent discharge license.
3. The bulk cost for delivered ferric chloride is \$0.20 per dry pound as FeCl_3 . The product is delivered as a 38 percent solution.
4. The bulk cost for delivered caustic (50% NaOH) is \$0.08 per pound.
5. Sludge age is 6.5 days.
6. 50% of FeCl_3 precipitates as $\text{Fe}(\text{OH})_3$.
7. The total volume of the aeration basins is 8.85 MG.
8. The total volume of the secondary clarifiers is 6.35 MG.
9. The cost for sludge disposal is \$25 per dry ton.

Figure 3: Total Phosphorus Removal from Filtered MLSS

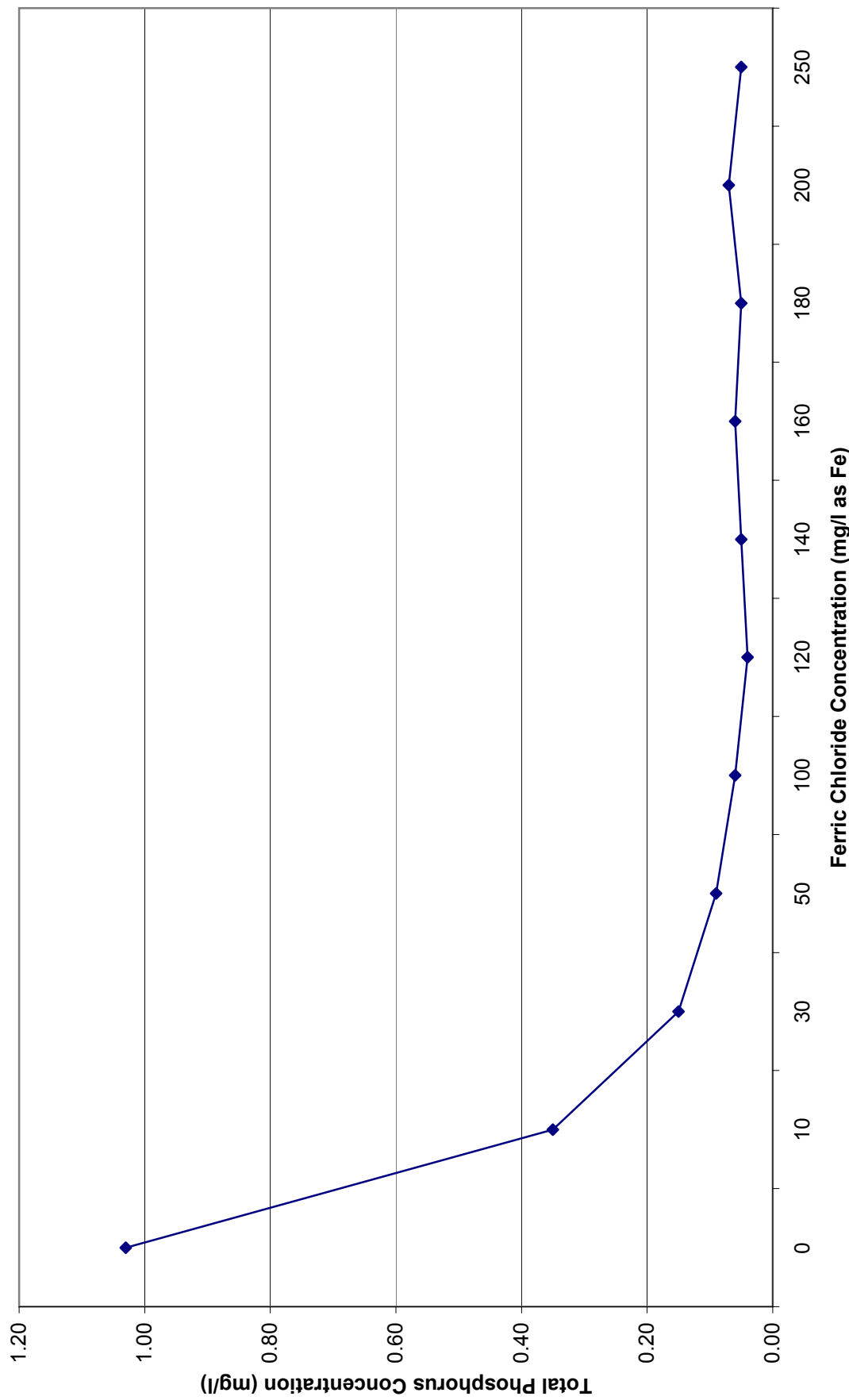


Table 1: Cost Estimate per Year

	120 mg-Fe/l	180 mg-Fe/l
FeCl ₃ addition cost	\$2,800,000	\$4,200,000
Caustic addition cost	\$442,000	\$442,000
Additional sludge disposal cost	\$57,000	\$89,000
Total Cost	\$3,300,000	\$4,700,000

Table 2: Quantities per Day

	120 mg-Fe/l	180 mg-Fe/l
4,500 gallon trucks of FeCl ₃	2-3	3-4
Increase in MLSS Conc. (mg/l)	1,730 mg/l	2,600 mg/l

Capital Cost

Due to the ferric hydroxide solids created from ferric chloride addition, additional inert solids would be added to the system. These would build up in the mixed liquor according to the sludge age of the biological treatment system. The treatment plant's MLSS concentration would be expected to increase by approximately 1,700 to 2,600 mg/l. The treatment plant is already operating near the upper limit of the preferred MLSS concentration to maintain a reasonable Food-to-Mass ratio and prevent excessive solids loading on the secondary clarifiers. Further, the bench testing demonstrated that ferric chloride would decrease settling rates in the secondary clarifier on the order of 30 to 45 percent. This would have an obvious detrimental impact on TSS removal, particularly during periods of high solids loading to the secondary clarifiers.

It is important to keep in mind that the laboratory testing provides results under ideal conditions (i.e. settling). To fully understand the effectiveness of the ferric chloride treatment, a full scale test at the MeadWestvaco treatment plant is strongly recommended. It is also recommended that, if a 0.25 mg/l total P limit were to be imposed on the mill, full-scale tertiary filtration would be required to guarantee consistent compliance with that limit. Since microbes contain P in their cell mass, such a limit would necessitate very high levels of consistent TSS removal. The capital cost of such a tertiary treatment system would range from \$15 to \$45 million, depending on design conditions and equipment selection.

Conclusions and Recommendations

The bench-scale testing results demonstrate that ferric chloride is effective in removing phosphorous from the mill's wastewater. The operational cost to remove phosphorus to levels below 0.25 mg/l levels is estimated between \$3 and \$5 million per year in chemical and sludge disposal costs.

The treatment plant's MLSS concentration would be expected to increase by approximately 1,700 to 2,600 mg/l, placing additional solids loading on a system already operating near the upper limit of the recommended Food-to-Mass Ratio and solids loading ranges. Secondary settling rates would decrease appreciably, negatively impacting TSS removal efficiency. To fully understand the effectiveness of the ferric chloride treatment, a full scale test at the MeadWestvaco treatment plant is strongly recommended.

It is also recommended that, if a 0.25 mg/l total P limit were to be imposed on the mill, full-scale tertiary filtration would be required to guarantee consistent compliance with that limit. Since microbes contain P in their cell mass, such a limit would necessitate very high levels of consistent TSS removal. The capital cost of such a tertiary treatment system would range from \$15 to \$45 million, depending on design conditions and equipment selection.

Woodard & Curran appreciates the assistance provided by MeadWestvaco during the site visit, especially the wastewater treatment plant operators, for their patience and use of their laboratory space.